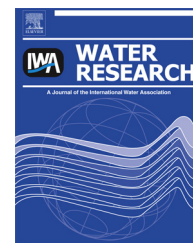


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Valorization of artichoke wastewaters by integrated membrane process

C. Conidi^a, A. Cassano^{a,*}, E. Garcia-Castello^b^a Institute on Membrane Technology, ITM-CNR, c/o University of Calabria, via P. Bucci, 17/C, I-87030 Rende, Cosenza, Italy^b Instituto Universitario de Ingeniería de Alimentos para el Desarrollo, Univesidad Politécnica de Valencia, Camino de Vera s/n, 46022 Valencia, Spain

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ABSTRACT

In this work an integrated membrane system was developed on laboratory scale to fractionate artichoke wastewaters. In particular, a preliminary ultrafiltration (UF) step, based on the use of hollow fibre membranes, was investigated to remove suspended solids from an artichoke extract. The clarified solution was then submitted to a nanofiltration (NF) step. Two different 2.5×21 in. spiral-wound membranes (Desal DL and NP030) with different properties were investigated. Both membranes showed a high rejection towards the phenolic compounds analysed (chlorogenic acid, cynarin and apigenin-7-O-glucoside) and, consequently, towards the total antioxidant activity (TAA). On the other hand, the Desal DL membrane was characterized by a high rejection towards sugar compounds (glucose, fructose and sucrose) (100%) when compared with the NP030 membrane (4.02%).

The performance of selected membranes in terms of permeate flux, fouling index and water permeability recovery was also evaluated.

On the base of experimental results, an integrated membrane process for the fractionation of artichoke wastewaters was proposed. This conceptual process design permitted to obtain different valuable products: a retentate fraction (from the NP030 membrane) enriched in phenolic compounds suitable for nutraceutical, cosmeceutical or food application; a retentate fraction (from the Desal DL membrane), enriched in sugar compounds, of interest for food applications; a clear permeate (from the Desal DL membrane) which can be reused as process water or for membrane cleaning.

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1. Introduction

The artichoke (*Cynara scolymus* L.) processing industry generates large amounts of agricultural solid wastes (leaves, stems, bracts of the artichoke plant) and wastewaters, such as blanching waters, which are not suitable for human consumption. These wastes are generally used as animal

feedstuff and for fibre production or directly discarded, with additional waste treatment costs in compliance with environmental laws (Llorach et al., 2002; Megias et al., 1999). In the search for new applications of artichoke wastes, it has been confirmed that they contain a large amount of bioactive compounds. Different studies have demonstrated their health-promoting potential, especially their hepatoprotective

* Corresponding author. Tel.: +39 (0)984 492067; fax: +39 (0)984 402103.
E-mail address: a.cassano@itm.cnr.it (A. Cassano).

(Adzet et al., 1987), antioxidative (Gebhardt, 1997), anticarcinogenic (Clifford, 2000), and hypocholesterolemic (Clifford and Walker, 1987) activities.

The pharmacological properties of artichoke are well documented in vivo and in vitro studies for the treatment of hepato-biliary dysfunction, dyspeptic syndromes, gastric diseases, as well as for the inhibition of cholesterol biosynthesis and low lipoprotein (LDL) oxidation, agents responsible for arteriosclerosis and coronary heart disease (Lattanzio et al., 2009). Artichoke leaf extracts decreased serum lipids, as well as hepatic and cardiac oxidative stress in rats fed on a high cholesterol diet (Kucukgergin et al., 2010).

The biological activity of artichoke by-products, and in particular their marked antioxidative effects, are linked to their special chemical composition, which includes high levels of phenolic compounds with a wide range of caffeoyl-quinic acid derivatives (with chlorogenic acid as the most important of these derivatives) and flavonoids such as apigenin-7-O-glucoside and luteolin (Abu-Reidah et al., 2013; Christaki et al., 2012; Mulinacci et al., 2004; Negro et al., 2002; Sanchez-Rabameda et al., 2003).

In addition, artichoke wastewaters contain inulin, a plant-derived carbohydrate which has been associated with enhancing the gastrointestinal and immune systems, increasing the absorption of calcium and magnesium and reducing the levels of cholesterol and serum lipids (Niness, 1999; Saengkanuk et al., 2011).

Due to these characteristics artichoke by-products represent a very useful source of high added value compounds of potential interest as food additives and nutraceuticals (Ceccarelli et al., 2010; Lattanzio et al., 2009).

Different methods to obtain purified extracts containing phenolic compounds from fruit or vegetable by-products have been evaluated including solvent extraction, γ -irradiation assisted extraction, hot water extraction, resin-based extraction, ultrasound-assisted extraction, enzyme-assisted extraction, and supercritical fluid extraction (Calvarano et al., 1996; Kim et al., 2008; Li et al., 2006; Xu et al., 2008). However, these extraction methods may either cause the degradation of the targeted compounds due to high temperature and long extraction times as in solvent extractions, or pose some health-related risks due to the unawareness of safety criteria during irradiation (Azmir et al., 2013). Furthermore, enzymes in enzyme-assisted extraction are easy to denature.

Therefore, efficient extraction methods, able to guarantee the stability of phenolic compounds are needed.

Pressure driven membrane processes, such as ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), have been successfully employed for the purification and concentration of bioactive compounds from natural products. These processes offer particular advantages in terms of absence of phase transition, mild operating conditions, possibility to avoid the use of additives, low energy requirement, separation efficiency and easy scaling up when compared with conventional methodologies. Successful applications related to the concentration and fractionation of grape phenolics (Crespo and Brazinha, 2010; Kalbasi and Cisneros-Zevallos, 2007; Nawaz et al., 2006), the concentration of coffee extract (Pan et al., 2013), the fractionation of bioactive compounds

extracted from propolis (Tsibranska et al., 2011) and the concentration of bioactive compounds from vegetable sources (Tylkowski et al., 2011) have been reported.

In this work, an integrated membrane process based on the use of UF and NF processes was investigated in order to fractionate artichoke wastewaters in high added value compounds, such as phenolic compounds and sugars. In particular, an aqueous artichoke extract was submitted to a preliminary cross-flow UF process devoted to the removal of suspended solids. The UF permeate was then processed by two different NF membranes in order to identify a suitable membrane able to separate phenolic compounds from sugars. The performance of both processes was evaluated in terms of productivity, fouling index, recovery of hydraulic membrane permeability and selectivity towards compounds of interest.

2. Material and methods

2.1. Artichoke wastewaters

Artichokes were purchased from a local open market (Cosenza, Italy). The vegetables were manually washed in water and cut in pieces. The aqueous extract of artichoke was obtained by heating the vegetable material (leaves, stems and fruits) in water at 85 °C for about 30 min, avoiding boiling.

2.5 kg of fresh vegetable material were placed in 10 L of tap water. The decoction solution was separated from the vegetable material by filtering it with a nylon cloth. The obtained liquor was stored at −17 °C and defrosted at room temperature before use.

2.2. Membrane filtration set-up and procedures

2.2.1. Ultrafiltration of artichoke wastewaters

Artichoke wastewaters were submitted to a preliminary UF process in order to remove suspended solids and macromolecular compounds and to reduce fouling phenomena in the subsequent NF process. UF experiments were performed by using a laboratory pilot unit supplied by Verind SpA (Milano, Italy). The UF system was operated at a transmembrane pressure (TMP) of 0.31 bar, an axial feed flow rate (Q_f) of 556 L/h and a temperature (T) of 24 ± 2 °C, according to the batch concentration mode (recycling the retentate stream and collecting the permeate separately) up to a volume reduction factor (VRF) of 5.67.

The volume reduction factor is defined according to Eq. (1):

$$\text{VRF} = \frac{V_f}{V_r} \quad (1)$$

where V_f and V_r are the initial volume of the feed and the retentate volume, respectively.

2.2.2. Nanofiltration of clarified artichoke wastewaters

The NF process was performed by using a laboratory plant supplied by Matrix Desalination Inc. (Florida, USA). The equipment consists of a feed tank with a capacity of 20 L, a stainless steel housing for 2.4×21 inches spiral wound membrane module, a high pressure pump, two pressure gauges (0–40 bar) for the control of the inlet and outlet

Table 1 – Properties of UF and NF membranes.

Membrane type	DCQ III-006C	NP030	Desal DL
Manufacturer	China Blue Star Membrane Technology	Microdyn Nadir	GE Water & Process Technologies
Configuration	Hollow fibre	Spiral wound	Spiral wound
Material	Polysulphone	Polyethersulfone	Cross-linked aromatic polyamide
NMWC0 (Da)	50,000	400	150–300
Maximum operating pressure (bar)	–	40	40
Maximum operating temperature (°C)	50	50	50
Na ₂ SO ₄ retention (%)	–	85–95	–
MgSO ₄ retention (%)	–	–	96
pH range	2–9	2–11	2–11
Effective membrane surface area (cm ²)	1.2	1.8	2.5
Volume fraction of small pores (%) ^a	–	53.7	18.8
Volume fraction of large pores (%) ^a	–	8.3	1.7
Contact angle (°)	–	82	46 ± 2

^a Data from literature (Boussu et al., 2008).

pressures, a pressure control valve and a coiling cool fed with tap water used to maintain the feed temperature constant.

Experimental runs were performed according to the batch concentration mode up to a final VRF of 5. The NF system was operated at a TMP of 8 bar and at a temperature of 25 ± 2 °C. The axial feed flow rate was fixed at 300 L/h for the NP030 membrane and 400 L/h for the Desal DL membrane, respectively.

Permeate and retentate samples were collected at different VRF values. They were stored at –18 °C and defrosted before the analyses.

2.3. Membranes, pure water permeability, fouling index and membrane cleaning

Artichoke wastewaters were clarified by using a hollow fibre ultrafiltration membrane module supplied by China Blue Star Membrane Technology Co., Ltd (Beijing China). The clarified liquor was then treated by using two different 2.5 × 21 inches spiral-wound NF membrane modules: NP030 (Microdyn Nadir, Germany) and Desal DL (GE Water & Process Technologies, USA). The characteristics of the selected membranes are reported in Table 1. Prior to the experimental runs with the artichoke wastewaters, water permeability coefficients (L_p) of selected membranes were determined by using deionized water at various operating pressures, according to the Eq. (2):

$$L_p = \frac{J_w}{\text{TMP}} \quad (2)$$

where J_w is the water flux (L/m²h) and TMP (bar) is the applied pressure difference across the membrane.

The fouling index (I_f) of selected membranes was evaluated by measuring the water permeability before and after the treatment with artichoke wastewaters according to the following equation:

$$I_f = \left(1 - \frac{L_{p1}}{L_{p0}}\right) \cdot 100 \quad (3)$$

where L_{p1} and L_{p0} are the water permeabilities (L/m²hbar) measured after and before the treatment with artichoke wastewaters, respectively.

After the treatment with artichoke solutions, UF and NF membranes were rinsed with tap water for 20 min and their water permeabilities were measured again. Then the UF membrane was submitted to an alkaline cleaning by using a NaOH solution at 0.1%(w/v), for 60 min at 40 °C, followed by an enzymatic cleaning with Ultrasil 50 (Henkel, Dusseldorf, Germany) at 1%(w/v) (60 min, 40 °C); NF membranes were cleaned only with the enzymatic solution in the same operating conditions. At the end of each cleaning procedures membranes were rinsed with tap water for 30 min and the water permeability was measured once again.

The water permeability recovery (WPR) was evaluated according to the following equation (Al-Amoudi and Lovitt, 2007):

$$\text{WPR} = \frac{L_{p2}}{L_{p0}} \cdot 100 \quad (4)$$

where L_{p2} is the water permeability measured after the chemical cleaning.

2.4. Analytical determinations

The suspended solids content was determined by centrifuging 10 mL of a pre-weight sample at 2000 rpm for 20 min; the weight of settled solids was determined after removing the supernatant.

Total soluble solids (TSS) were measured by an Abbe refractometer Bellingham + Stanley 60/DR (Bellingham + Stanley Ltd., Kent, UK) at 20 °C.

The content of polyphenols was determined by a Waters Alliance 2695 HPLC system (Milford, MA, USA) equipped with a vacuum degasser, a binary pump, an autosampler, a thermostated column compartment, a model 2996 diode array detector (DAD) and an Empower software (Waters Corporation, Milford, Ireland) for data collection.

Chromatographic separation was performed by using a Luna C 18(2) column (250 × 4.6 mm, 5 μm) supplied by Phenomenex (Torrance, CA, USA). The mobile phase consisted of 0.1% of HCOOH in water (eluent A) and 0.1% of HCOOH in acetonitrile (eluent B). The following gradient system was

Table 2 – Chemical composition of artichoke wastewaters.

Suspended solids (%)	2.5 ± 0.10
TSS (°Brix)	3.05 ± 0.05
Glucose (mg/L)	960 ± 1
Fructose (mg/L)	837 ± 1.07
Sucrose (mg/L)	1050 ± 0.41
TAA (mM Trolox)	8 ± 0.042
Chlorogenic acid (mg/L)	251 ± 2.64
Cynarin (mg/L)	164.7 ± 1.41
Apigenin-7-O-glucoside (mg/L)	101 ± 2

used: 0 min, 90% A and 10% B; 30 min, 50% A and 50% B; 35 min, 0% A and 100% B. Analyses were stopped after 50 min. The system was equilibrated between different runs for 10 min using the start mobile phase composition. The flow was maintained at 1 mL/min and the injection volume was 10 µL. Diode array detection was between 200 and 600 nm.

Prior to HPLC analysis all samples were filtered by using 0.45 µm nylon filters. All polyphenols were identified by matching the retention time and their spectral characteristics against those of standards. Quantification was made according to the linear calibration curves of standard compounds.

Analyses of sugars were performed by a high performance anion exchange chromatography coupled with pulsed amperometric detection (HPAEC-PAD). The separation was performed by using a Metrosep Car B column (250 × 4.6 mm) from Metrohm (Herisau, Switzerland). The following conditions were used: flux, 1 mL/min; detector temperature, 32 °C; pressure, 9–10 MPa; mobile phase, NaOH 0.1 M (isocratic elution). Prior to HPAEC analysis all samples were filtered by using 0.45 µm nylon filters and diluted 1:25 with bidistilled water.

The total antioxidant activity (TAA) was measured using the method described by [Arnous et al. \(2001\)](#). An aliquot of 0.2 mL of diluted sample was added to 3.8 mL of a DPPH (2,2-diphenylpicrylhydrazyl) solution (60 µM in CH₃OH) and vortexed. The absorbance was measured at $t = 0$ and $t = 30$ min at 515 nm. The antioxidant capacity was determined as a percentage of inhibition of the DPPH radical (I_{DPPH}) according to the following equation:

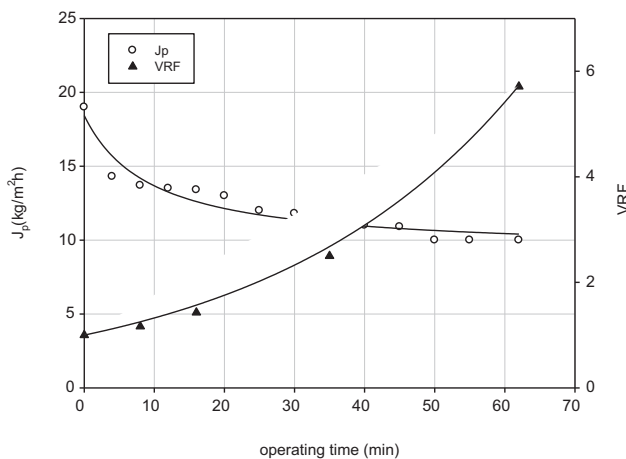


Fig. 1 – Ultrafiltration of artichoke wastewater. Time course of permeate flux and VRF (Operating conditions: TMP, 0.31 bar; Qf, 556 L/h; T, 24 ± 2 °C).

Table 3 – Water permeability, fouling index and permeability recovery of UF and NF membranes.

Membrane type	L_{p0} (L/m ² hbar)	L_{p1} (L/m ² hbar)	L_{p2} (L/m ² hbar)	I_f (%)	WPR (%)
DCQ III-006C	210.44	50	185.3	76.5	88
NP030	3.41	2.0	2.6	41	76.5
Desal DL	3.56	3.5	3.56	1.7	100

$$I_{DPPH} = \left(\frac{A_{c(0)} - A_{A(30)}}{A_{c(0)}} \right) \cdot 100 \quad (5)$$

where $A_{c(0)}$: absorbance of the control at $t = 0$ min and $A_{A(30)}$: absorbance of the antioxidant at $t = 30$ min. Results were expressed as mM Trolox equivalent.

All measurements were performed in triplicate. Results were expressed as mean value ± SD.

The rejection (R) of UF and NF membranes towards specific compounds was calculated as follows:

$$R = \left(1 - \frac{C_p}{C_f} \right) \cdot 100 \quad (6)$$

where C_f and C_p are the concentration of a specific component in the permeate and feed, respectively.

The adsorbed phenolic amount Q_{ADS} (mg/m²) on the membrane surface at different VRF values was determined as follows ([Saleh et al., 2006](#)):

$$Q_{ADS} = \frac{C_f V_f - (C_r V_r + C_p V_p)}{A} \quad (7)$$

where V_f , V_r and V_p are the feed, retentate and permeate volumes, respectively; C_r is the concentration of phenolic compounds in the retentate and A the membrane surface area.

3. Results and discussion

3.1. Composition of artichoke wastewaters

The general composition of artichoke wastewaters submitted to the UF treatment is reported in [Table 2](#). The HPLC chromatogram related to the analysis of polyphenols highlights the presence of the chlorogenic acid and apigenin 7-O-glucoside as the most important phenolics compounds. The content of chlorogenic acid of the UF feed was of about

Table 4 – Chemical composition of artichoke wastewaters before and after the clarification with the UF membrane.

Parameters	Feed	Permeate	Retentate
Suspended solids (%)	2.5 ± 0.10	n.d.	2.43 ± 0.10
TSS (°Brix)	3.05 ± 0.05	2.94 ± 0.065	3.11 ± 0.07
Glucose (mg/L)	960 ± 1	958 ± 0.93	966 ± 0.66
Fructose (mg/L)	837 ± 1.07	830 ± 2.5	840 ± 1.70
Sucrose (mg/L)	1050 ± 0.41	1040 ± 0.49	1055 ± 0.6
TAA (mM Trolox)	8 ± 0.042	7.9 ± 0.04	8.2 ± 0.3
Chlorogenic acid (mg/L)	251 ± 2.64	245 ± 4.6	250.6 ± 1.52
Cynarin (mg/L)	164.7 ± 1.41	161 ± 1.1	162.6 ± 1.52
Apigenin-7-O-glucoside (mg/L)	101 ± 2	100 ± 4.5	100.4 ± 2.9

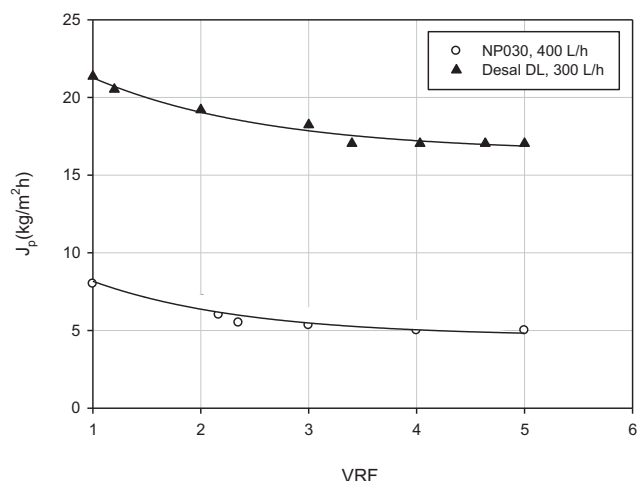


Fig. 2 – Nanofiltration of clarified artichoke wastewaters. Evolution of permeate flux as a function of VRF (Operating conditions: TMP, 8 bar; T, 24 ± 2 °C).

250 mg/L. A similar value was observed by Schutz et al. (2004) in samples (defined as artichoke juices) prepared from freeze-dried artichoke heads and pomace extracted with aqueous methanol (60%, v/v); on the contrary, a higher content of apigenin-7-O-glucoside was found in the UF feed (about 100 mg/L) if compared with the juice (61 mg/L).

The TAA of artichoke wastewaters was of about 8 mM Trolox (% inhibition of DPPH radical of 16.5%) due to the presence of different antioxidant compounds. In particular, as main antioxidant compounds in *Cynara cardunculus* extracts Kukić et al. (2008) identified apigenin and luteolin, and their glycosides, as well as chlorogenic acid. A neuroprotective activity of chlorogenic acid together with a marked inhibition of lipid peroxidation was identified by Nakajima et al. (2007).

3.2. Clarification of artichoke wastewaters

Fig. 1 shows the productivity of the UF membrane in terms of kg of permeate produced per unit area and time (kg/m²h) in

the treatment of artichoke wastewaters, in selected operating conditions, up to a VRF of 5.74. The initial permeate flux was of about 19 kg/m²h; it decreased during the process by increasing the VRF due to concentration polarization, fouling phenomena and increased concentration of solutes in the retentate. A state-steady permeate flux of about 10 kg/m²h was obtained at a VRF of 3.

After two cleaning steps with alkaline and enzymatic solutions, the initial water permeability ($L_{p0} = 210.44 \text{ L/m}^2\text{h}$) of the UF membrane was not completely recovered. In particular, the cleaning with the NaOH solution permitted to recover 65% of the initial water permeability; the following enzymatic cleaning step permitted to recover about 88% of the initial water permeability of the membrane (Table 3). The incomplete recovery of the initial hydraulic permeability could be attributed to an irreversible component of fouling.

The chemical composition of permeate and retentate streams obtained in the UF treatment of artichoke wastewaters is reported in Table 4. The UF treatment permitted to preserve different bioactive compounds (chlorogenic acid, cynarin and apigenin-7-O-glucoside), TAA and sugars (glucose, fructose, sucrose) in the permeate fraction due to the low rejection measured (in the range 1.2–8.6%), while suspended solids were completely retained in the retentate side ($R = 100\%$).

3.3. Nanofiltration of clarified artichoke wastewaters

The UF permeate was processed by using two different NF membranes. Fig. 2 shows the evolution of the permeate flux as a function of VRF for both NF membranes in the selected operating conditions. The Desal DL membrane showed higher permeate fluxes compared with the NP030 membrane, also considering its lower nominal MWCO: the initial permeate flux was of about 21 kg/m²h; it decreased at a steady-state value of 18 kg/m²h when the VRF reached a value of 3. For the NP030 membrane, a lower steady-state permeate flux (5 kg/m²h) was measured.

Similar results were reported by Cissè et al. (2011) during the treatment of roselle extract with the same NF membranes.

Table 5 – Evaluation of polyphenols in different samples coming from the NF treatment.

Membrane type	Sample	VRF	Cynarin (mg/L)	Chlorogenic acid (mg/L)	Apigenin-7-O-glucoside (mg/L)
Desal DL	Feed		158 ± 2.5	240 ± 2.15	100.6 ± 3.10
	Permeate	2,3,4,5	n.d.	n.d.	n.d.
	Retentate	2	200 ± 2.1	310 ± 5.3	205 ± 2.0
		3	250 ± 4.6	510 ± 2.12	312 ± 3.46
		4	400 ± 6.0	620 ± 2.0	380 ± 1.10
5		450 ± 5.88	700 ± 1.70	480 ± 2.55	
NP030	Feed		158 ± 2.3	246.5±1.7	100.2 ± 2.9
	Permeate	2	16 ± 2.1	13.2±2.4	19 ± 2.2
		3	15.2 ± 1.4	13 ± 2.6	19.2 ± 1.3
		4	15 ± 1.6	12.5 ± 3.4	19 ± 1.7
		5	14 ± 1.0	10 ± 1.74	18 ± 2.1
	Retentate	2	256 ± 4.0	385 ± 4.35	180 ± 6.1
		3	312 ± 1.9	456 ± 3.6	256 ± 2.0
		4	350 ± 1.0	572 ± 2.4	325 ± 5.0
		5	412 ± 2.8	612 ± 2.4	400 ± 2.6

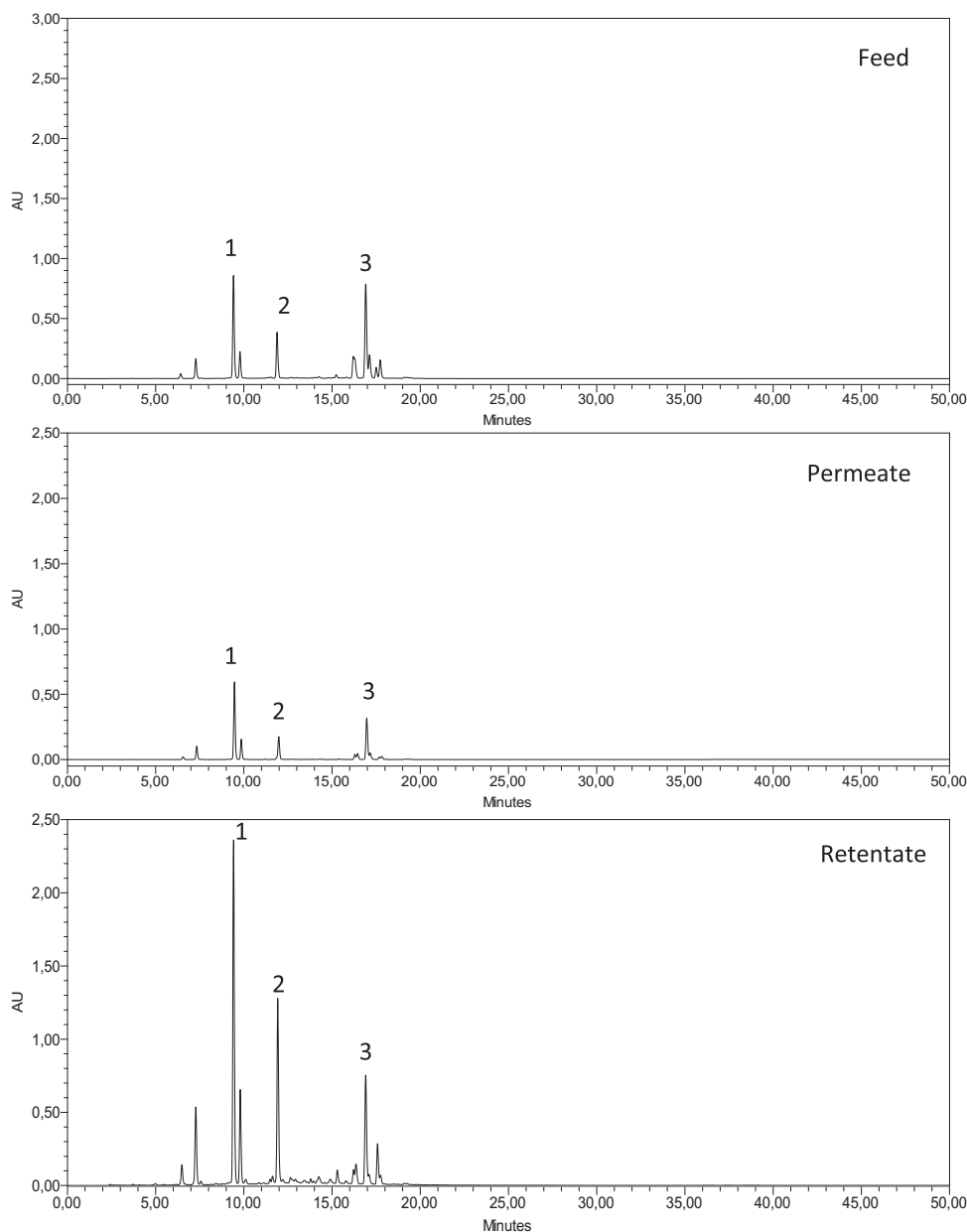


Fig. 3 – HPLC chromatograms of phenolics compounds detected in feed, permeate and retentate samples coming from the NF process with the NP030 membrane (VRF = 5). Peak 1: chlorogenic acid; 2: cynarin; 3: apigenin-7-O-glucoside.

Particularly, the Desal DL membrane presented higher permeate fluxes ($40 \text{ kg/m}^2\text{h}$) in comparison with the NP030 membrane characterized by average permeate fluxes of $5.75 \text{ kg/m}^2\text{h}$. These results confirm that permeate fluxes are affected by membrane material and structure, as well as by interactions between solute and membrane. Boussu et al. (2008) observed that the adsorption of uncharged organic components on hydrophobic and smooth membranes with a high MWCO and a porous polyethersulfone (PES) top layer (such as the NP030 membrane), was higher when compared with membranes having a top layer in polyamide (such as the Desal DL membrane).

For both investigated membranes the flux decline up to the final VRF value was limited by the UF pre-treatment. In particular, permeate flux reductions of 20.4% and 37.5% were

evaluated for the Desal DL and the NP030 membrane, respectively. These differences can be explained assuming a different porosity of the top layer (expressed as the volume fraction of small and large pores, respectively) of both membranes, as reported in Table 1. According to the results of Boussu et al. (2008), a low volume fraction of small pores (as for the Desal DL membrane) is desirable in the case of feed solutions containing dissolved uncharged or charged organic components to minimize fouling phenomena.

These results are also in agreement with the fouling index values measured for both selected membranes on the base of their water permeability before and after the treatment of clarified artichoke wastewaters. The NP030 membrane showed a higher fouling index (41%) in comparison with the Desal DL (1.7%) (Table 3).

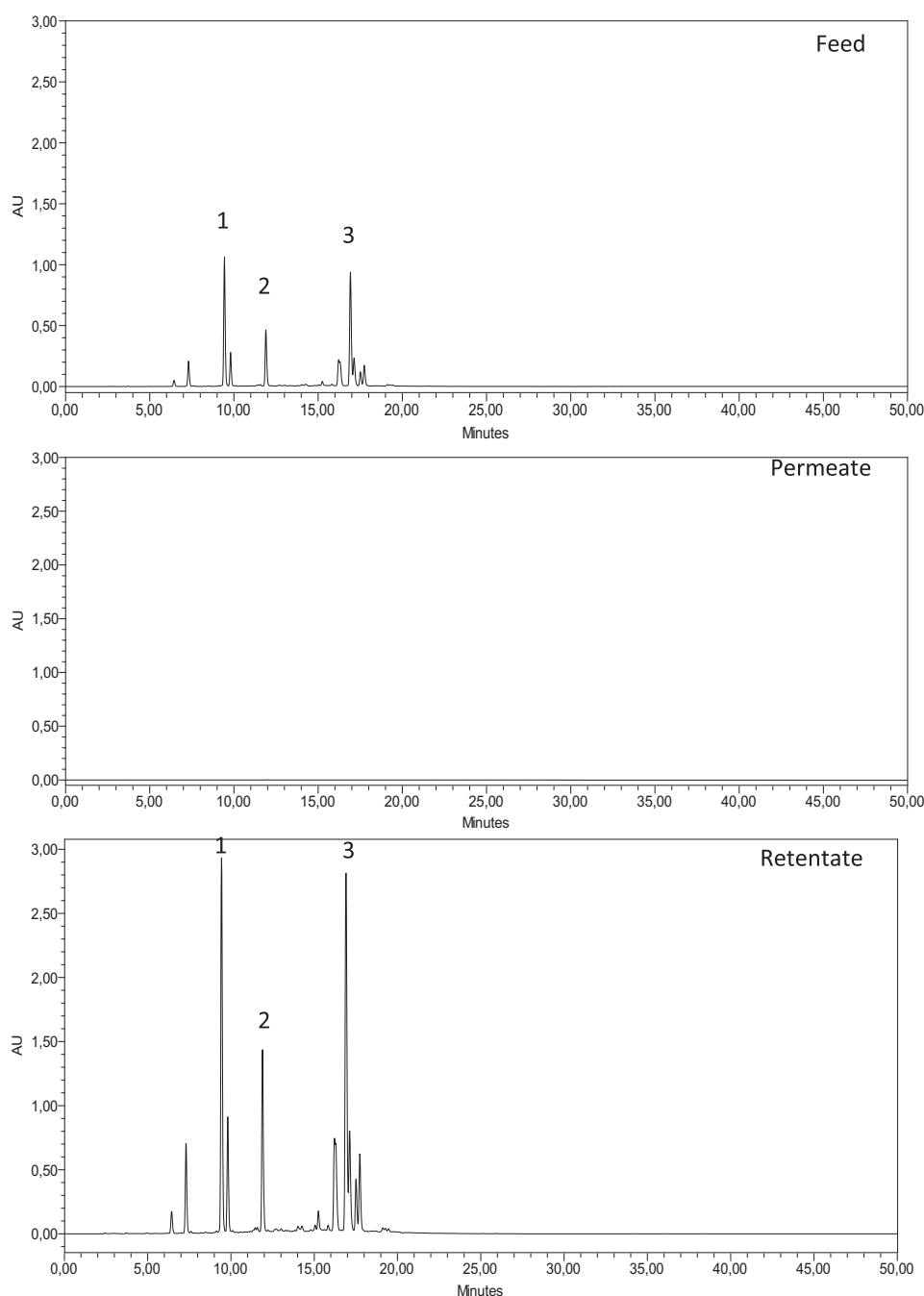


Fig. 4 – HPLC chromatograms of phenolics compounds detected in feed, permeate and retentate samples coming from the NF process with the Desal DL membrane (VRF = 5). Peak 1: chlorogenic acid; 2: cynarin; 3: apigenin-7-O-glucoside.

The water permeability recovery, after the enzymatic cleaning, was of 100% for the Desal DL membrane and of 76.5% for the NP030 membrane, indicating for this membrane the presence of an irreversible component of fouling.

In Table 5 the content of phenolic compounds in permeate and retentate fractions of both NF membrane processes, at different VRF values, is reported. The concentration of analysed compounds in the retentate fractions increases by increasing the VRF in the range of values investigated. At VRF 5 the concentration of phenolic compounds in the retentate fraction of the Desal DL membrane is higher than the one

observed for the NP030 membrane. This behaviour can be attributed to the higher rejection of the Desal DL membrane towards phenolic compounds. Phenolic compounds were not detected in the permeate stream of the Desal DL membrane independently on the VRF value. According to its higher MWCO the NP030 membrane showed a lower rejection towards phenolic compounds (in the range of 82–96%).

HPLC chromatograms of phenolic compounds in feed, permeate and retentate streams of Desal DL and NP030 membranes, at VRF 5, are illustrated in Figs. 3 and 4, respectively. The permeate stream of the Desal DL

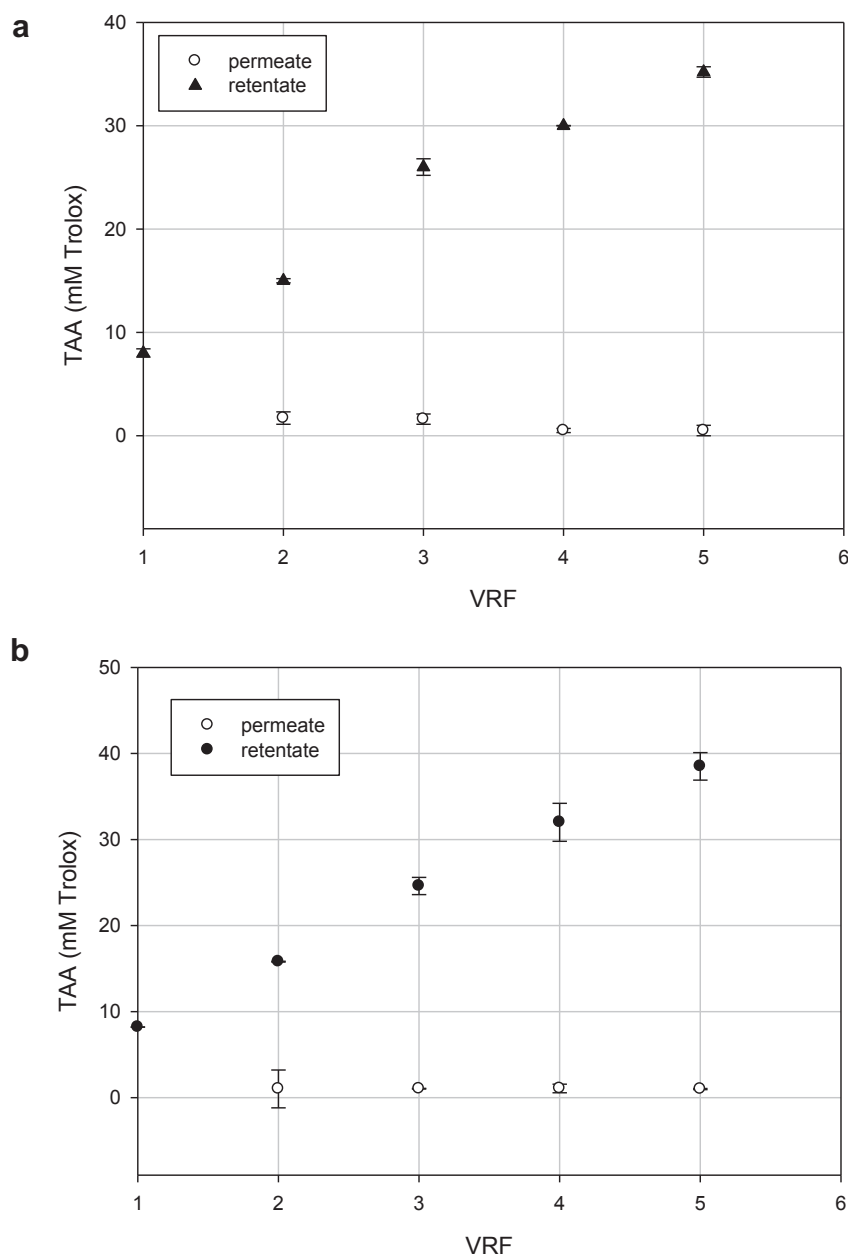


Fig. 5 – Antioxidant activity in permeate and retentate fractions of NF membranes as a function of VRF. a) membrane Desal DL; b) membrane NP030.

membrane results clearly depleted in phenolic compounds (Fig. 4).

These results are also in agreement with the determination of TAA. In particular, an increasing of TAA in the

retentate fractions of both NF membranes was observed by increasing the VRF (Fig. 5a and b). On the contrary, the TAA in the permeate stream was not influenced by the VRF value. The observed rejection of the TAA at VRF 5 was of

Table 6 – Evaluation of sugars in the different samples coming from the NF treatment (at VRF = 5).

Membrane type	Sample	Glucose (mg/L)	Fructose (mg/L)	Sucrose (mg/L)
Desal DL	Feed	920 ± 2	810 ± 0.02	1020 ± 0.1
	Permeate	n.d	n.d	n.d.
	Retentate	3937 ± 0.2	2877 ± 6	4382 ± 0.05
NP030	Feed	940 ± 0.01	813 ± 0.1	1038 ± 2
	Permeate	890 ± 1	786 ± 0.05	1002 ± 6.2
	Retentate	200 ± 1	256 ± 0.5	112 ± 2.4

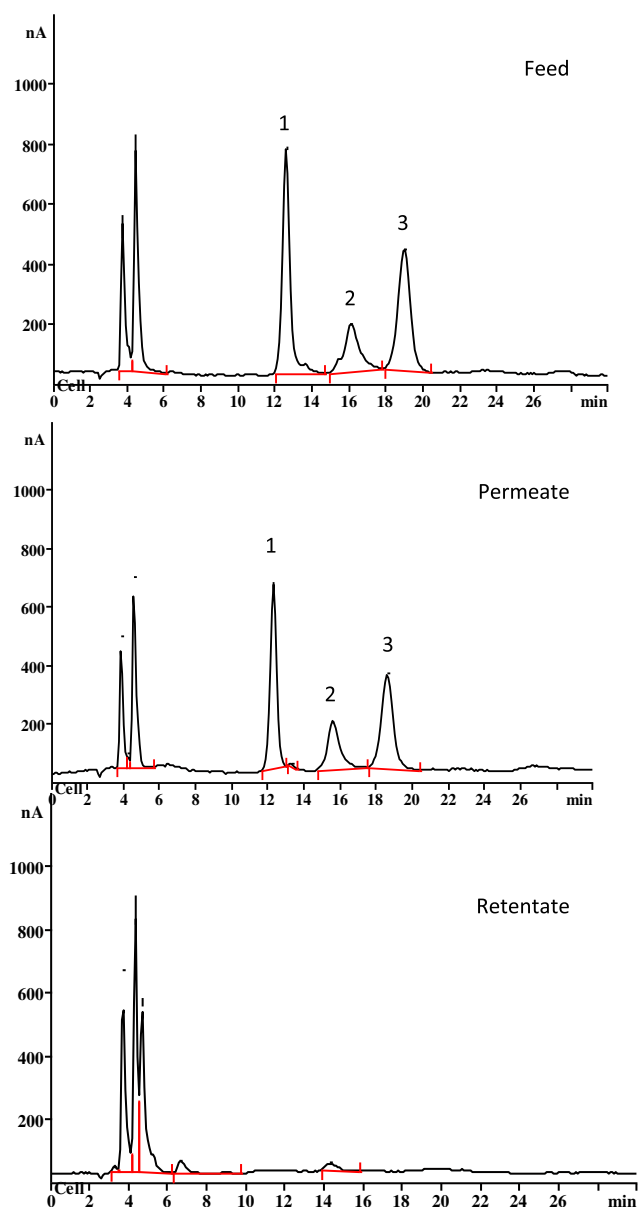


Fig. 6 – HPAEC chromatograms of sugars detected in feed, permeate and retentate samples coming from the NF process with the NP030 membrane. Peak 1: glucose; 2: fructose; 3: sucrose.

93.7% for the Desal DL membrane and 87.8% for the NP030 membrane.

A significant increase of phenolic compounds and antioxidant activity by increasing the VRF was also reported by Prudêncio et al. (2012) in the treatment of mate bark aqueous extracts with a spiral-wound NF membrane (GE Desal HL2521TF) characterized by an approximate MWCO of 150–300 Da. Similarly to the data obtained with the Desal DL membrane, there were no total phenolic compounds detected in any of the permeate analysed at different VRF values.

In Table 6 the analysis of sugars (fructose, glucose and sucrose) in permeate and retentate fractions obtained at VRF 5 for both NF membranes are reported. It is interesting to note that in the permeate of the Desal DL membrane sugars were

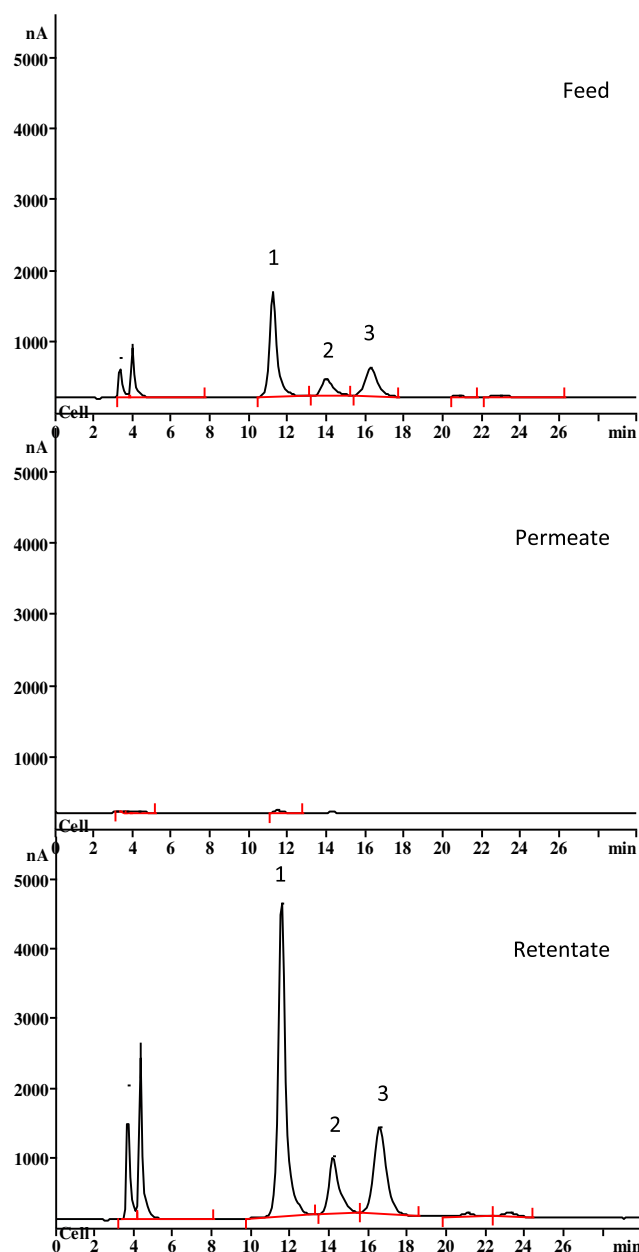


Fig. 7 – HPAEC chromatograms of sugars detected in feed, permeate and retentate samples coming from the NF process with the Desal DL membrane. Peak 1: glucose; 2: fructose; 3: sucrose.

not detectable, while most of the initial sugar content in the clarified artichoke wastewater (permeate UF) can be recovered in the permeate of the NP030 membrane.

HPAEC chromatograms of sugars show that the NP030 membrane preserved the sugars in the permeate side, while the Desal DL membrane retained all the sugars in the retentate side (Figs. 6 and 7). A similar behaviour was observed by Kuhn et al. (2011) in the selection of NF membranes for the purification of fructooligosaccharides. The observed rejection of Desal DL membrane towards glucose, in a dead-end stirred cell filtration, was of 92%, while the NP030 membrane in the same conditions showed a rejection of 12%.

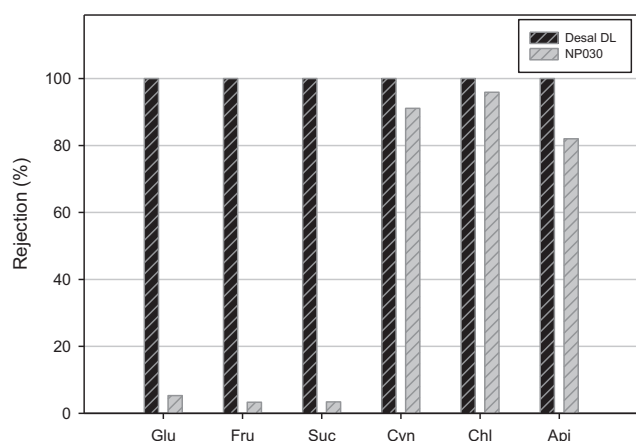


Fig. 8 – Rejections of NF membranes towards sugars and phenolic compounds (glu: glucose; fru: fructose; suc: sucrose; chl: chlorogenic acid; cyn: cynarin; api: apigenin-7-O-glucoside).

Fig. 8 summarizes the effect of NF membranes on the rejection of sugars and phenolic compounds. The Desal DL membrane showed a rejection of 100% towards the analysed compounds: this is in agreement with the MWCO of this membrane (150–300 Da) and the molecular weight of sugars and phenolic compounds (in the range of 516–180 g/mol).

The high rejection of the NP030 membrane towards phenolic compounds could be attributed to their adsorption on the membrane surface. As reported in Fig. 9, the level of adsorption of phenolic compounds at different VRF values, relative to the specific membrane surface area membrane, was lower for the Desal DL membrane than for NP030 membrane. For both membranes levels of adsorbed apigenin-7-O-glucoside were lower than those observed for cynarin and chlorogenic acid. In addition, at VRF 5 the NP030 membrane showed also a greater adsorption of sugar compounds.

The more hydrophobic character of the NP030 membrane, with a top layer in PES material, enhances the adsorption of

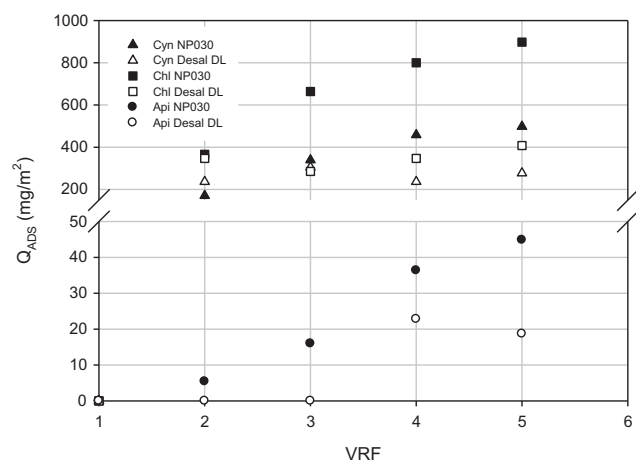


Fig. 9 – Adsorbed phenolics amount as a function of VRF for NP030 and Desal DL membranes (chl: chlorogenic acid; cyn: cynarin; api: apigenin-7-O-glucoside).

phenolic compounds on the membrane surface and the formation of a hydrophobic layer onto the membrane surface (Sotto et al., 2013) causing lower permeate fluxes and a higher fouling index in comparison with the Desal DL membrane (see Table 3). Susanto et al. (2009) supported the existing of benzene ring-benzene ring interactions to justify a greater amount of phenolic compounds adsorbed by PES membranes in comparison with more hydrophobic membranes such as those made in polypropylene. The formation of hydrogen bonds between the additive poly(vinyl)pyrrolidone (PVP) usually used in the manufacturing process and phenolic compounds was also confirmed.

3.4. Integrated membrane process

On the base of the obtained results, an integrated membrane process for the fractionation and recovery of valuable compounds starting from artichoke wastewaters is proposed (Fig. 10). The process scheme is based on a preliminary clarification of artichoke wastewaters by UF membranes followed by two NF steps: a first NF process separating sugars from phenolic compounds carried out with a PES membrane having a MWCO of 400 Da (such as the NP030 membrane); the retentate of this process is a fraction enriched in polyphenols, with a high value of the TAA (about 38 mM Trolox), of interest for pharmaceutical and/or food applications; the permeate stream, enriched in sugar compounds, can be processed by a polyamide NF membrane with a lower MWCO (i.e. 150–300 Da, such as the Desal DL membrane) in order to obtain a water stream (permeate fraction) which can be reused as processing water in the artichoke industry or for membrane cleaning and a retentate fraction enriched in sugars of interest for food applications.

4. Conclusions

A membrane-based process to fractionate the artichoke wastewaters in high added value compounds for different applications was investigated on laboratory scale.

A preliminary clarification step, performed by hollow fibre UF membranes, permitted to remove most suspended solids in the raw water. The clarified solution was then treated with two different NF membranes (Desal DL and NP030) showing a different selectivity towards phenolic compounds and sugars.

On the base of experimental results, a conceptual membrane-based process design for the fraction of artichoke wastewaters was proposed. The process allows to produce three different valuable fractions: a retentate fraction with high antioxidant activity due to the retention of phenolic compounds of potential interest for nutraceutical, cosmetic or food applications; a retentate fraction enriched in sugar compounds of interest for food applications; a clear permeate reusable as process water or for membrane cleaning.

The proposed process leads to significant advantages in terms of reduction of environmental impact, recovery of high added-value compounds, saving of water and energy requirements.

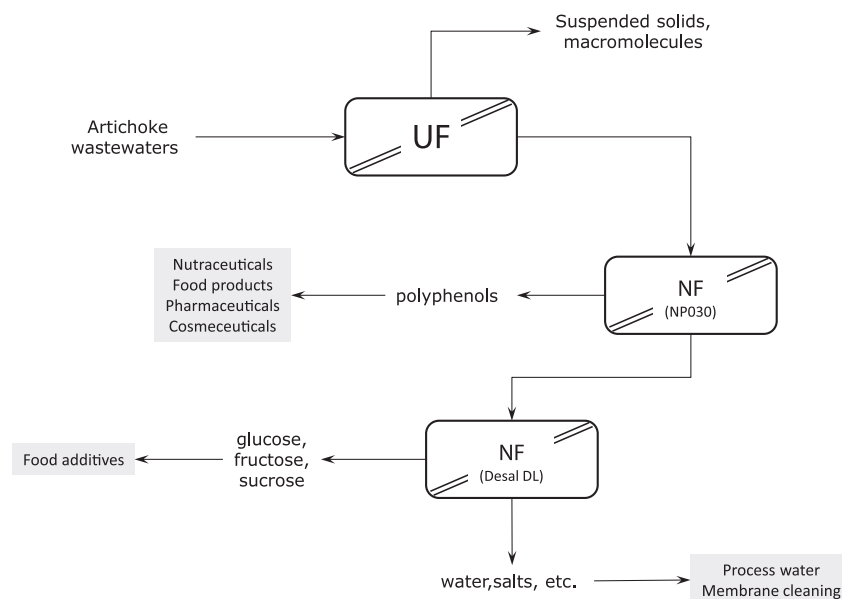


Fig. 10 – Conceptual process design for the treatment of artichoke wastewaters based on UF and NF operations.

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